Collision Lifetimes and the Thermodynamics of Real Gases*

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The perfect gas law $p/kT=n=\Sigma_i n_i$ (where n_i is in molecules per cm³) is inadequate for describing real gases because of the interactions during collisions. By a simple intuitive argument, these interactions can be taken into account exactly if you know the collision lifetimes. The product of collision rate and lifetime gives the concentration of transient collision complexes, which must be considered in the perfect gas law along with the stable species. As a result, the complete virial expansion is obtained, in both quantal and classical mechanics. The argument leads further to a new form for the partition function which includes the continuum as well as bound states. From this all the thermodynamic functions can be obtained.

A. EQUATION OF STATE

THE equation of state of real gases involves deviations from the perfect-gas law,

$$p/kT = n = \sum_i n_i, \qquad (1)$$

where n is measured in molecules per cm³ and the n_i refer to different species in the gas. The deviations caused by the formation of bound molecules from the parent gas can be handled by introducing the proper equilibria, and the various excited states of the parent species in the gas can be taken into account similarly. Each of the excited states can then be given a separate concentration n_i in the sum in Eq. (1).

Another class of interactions which also contribute to deviations from the perfect gas law are the interactions between two or more unbound molecules of the gas—these include the repulsive interactions that in the simplest case appear as the excluded volume in the van der Waals equation of state, and the attractive interactions that may result in the formation of metastable clusters ranging from a transient orbiting pair to the long-lived but unstable molecules that participate in unimolecular reaction processes. The effects of these interactions appear in the virial expansion of the gas law, and various devices have been used to compute the virial coefficients. In this note I try to carry through a simple intuitive approach that connects the gaseous equation of state with the lifetime matrix of collision theory. Truly bound molecules and excited states can be ignored and attention focused on the collisional interactions.

The lifetime matrix[1] provides a tool for analyzing each collision into a free-flight portion and a collision lifetime, which incorporates all the effects of the interaction. The free-flight portion corresponds to continued motion of the particles as if the interaction had not occurred (in the case of an inelastic collision, an instantaneous switch from an incoming to an outgoing free-flight path is assumed). The collision lifetime is always uniquely defined—it may even be negative, if the colliding particles separate sooner than they would have in free flight without interaction. The collision lifetime is well defined in the classical limit as well as quantally, but I use the quantal form with its relation to the scattering matrix since quantal effects are often important in molecular collisions. The collision lifetime is well defined for interactions of short range; it diverges for the Coulomb interaction, but may be defined for a shorter range interaction superimposed on the Coulomb, leaving the contribution of the Coulomb part to be dealt with otherwise. The gas is assumed dilute enough so that ordinary Boltzmann statistics can be used.

The basic idea of this article is to assume that a pair of molecules involved in any collision act like a single bound molecule for the duration of the collision lifetime and are completely free the rest of the time. The effective concentrations c_j of these collision complexes can be computed if their lifetimes are known, and they can be inserted in the sum on the right-hand side of Eq. (1) along with the stable species,

$$n = \sum_i n_i + \sum_j c_j. \qquad (2)$$

In doing this it must be remembered that the concentrations of the free stable species are reduced to the extent that they are transiently tied up in the complexes. Since the collision complex may have a negative lifetime, its concentration may be negative—but in this case the concentrations of its parents are effectively *increased*; this is, in fact, the result to be expected classically because of the excluded volume when the interaction is repulsive.

For example, if the collision occurs between molecules A and B, with initial concentrations $n_A{}^0$ and $n_B{}^0$, the reaction is

$$A + B \leftrightarrow (AB)_{complex}, \qquad (3)$$
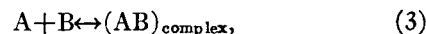
and the concentrations are

$$c_{AB}, \qquad n_A = n_A{}^0 - c_{AB}, \qquad n_B = n_B{}^0 - c_{AB}. \qquad (4)$$

[1] F. T. Smith, Phys. Rev. **118**, 349 (1960). See reference 2 for the correction of an error.

As a result the right-hand side of Eq. (1) becomes

$$n = n_A + n_B + c_{AB} = n_A{}^0 + n_B{}^0 - c_{AB}, \qquad (5)$$

which will be larger than $n^0 = n_A{}^0 + n_B{}^0$ if c_{AB} is negative. Clearly there is no chance for n itself to become negative.

We now wish to relate the concentrations c_j to the n_i and the lifetimes. What is needed is an equilibrium coefficient connecting c_j and the n_i:

$$c_j = c_{ik} = G_{ik}(T) n_i n_k. \qquad (6)$$

The equilibrium coefficient $G_{ik}(T)$ may of course be negative, and will be so in general if the interaction is predominantly repulsive. $G_{ik}(T)$ is just the equilibrium concentration of complexes in the presence of unit concentrations n_i, n_k of the parent species.

The connection with the collision lifetimes comes about because the concentration of an unstable complex is just the product of its rate of formation and its lifetime. The relationship has already been used in connection with a discussion of reaction rates and collision rates.[2] The collision lifetime for any colliding pair A_i, A_k depends not only on their internal states (which must be assumed to be completely specified by i, k) but also on the angular momentum quantum numbers l, m_l and the energy E of relative motion:

$$Q_{ik}(E, l, m_l). \qquad (7)$$

Assuming unit concentrations of the colliding partners, the rate of production of this complex with energy in the range $(E, E+\delta E)$ and in the given angular momentum state l, m_l is[2]

$$k(E, l, m_l)\delta E = (h^2/2\pi\mu kT)^{\frac{1}{2}} h^{-1} \exp(-E/kT)\delta E. \qquad (8)$$

The concentration of the complex in the range $(E, E+\delta E; l, m_l)$ is the product of this with the lifetime:

$$g_{ik}(E, l, m_l)\delta E = Q_{ik}(E, l, m_l) k(E, l, m_l)\delta E. \qquad (9)$$

The total concentration of this complex is then

$$G_{ik}(T) = \int_0^\infty \sum_{l,m_l} g_{ik}(E, l, m_l) dE$$

$$= \left(\frac{h^2}{2\pi\mu kT}\right)^{\frac{1}{2}} h^{-1} \sum_{l,m_l} \int_0^\infty Q_{ik}(E, l, m_l)$$

$$\times \exp(-E/kT) dE. \qquad (10)$$

It is easy to see that the infinite sum in l converges, because the interaction and the lifetime vanish at large values of l (or large impact parameters).

The lifetime $Q_{ik}(E, l, m_l)$ that enters into Eq. (10) is actually one of the diagonal elements of the lifetime matrix of reference 1, and it can be derived from the scattering matrix for the system. In the special case

[2] F. T. Smith, J. Chem. Phys. **36**, 248 (1962).

where A_i and A_k are spherically symmetric atoms, Q becomes simply the energy derivative of the phase shift and is independent of m_l:

$$Q(E, l, m_l) = 2\hbar(d\delta_l/dE). \qquad (11)$$

When this is inserted in Eq. (10) we encounter an expression which was first derived (by a different argument) by Kahn and Uhlenbeck[3] for the second virial coefficient for an atomic gas.

As the density of a gas is increased, higher-order complexes become important. These can be handled in just the same way as the two-body complexes, by introducing the collision lifetime and the collision rate for n-body collisions. The lifetime matrix for these cases has just been discussed elsewhere,[4] and the collision rate expressions are to be found in reference 2. By an argument similar to that followed in deriving Eq. (10) we can find its generalization to an n-body collision equilibrium:

$$G_{ij\ldots l}{}^{(n)*}(T) = \left(\frac{h^2}{2\pi\mu kT}\right)^{\frac{1}{2}(n-1)} h^{-1} \int_0^\infty \sum_\gamma Q_{ij\ldots l}{}^{(n)}(E, \gamma)$$

$$\times \exp(-E/kT) dE. \qquad (12)$$

(The reason for writing G^* will become apparent later.) Here γ is a set of $3n-4$ quantum numbers for the generalized orbital angular momentum of the n-body collision[5] and μ is the n-body reduced mass,

$$\mu^{n-1} = \prod_i m_i / \sum_i m_i. \qquad (13)$$

From $G^{(n)*}$ we can now obtain an apparent concentration for n-body complexes,

$$c_{i,j\ldots, l}{}^{(n)*} = G_{i,j\ldots, l}{}^{(n)*}(V) n_i n_j \cdots n_l. \qquad (14)$$

However, caution must be adopted in using this expression, because of a contribution of lower-order collision complexes to the lifetime $Q^{(n)}$ that went into the definition of $G_{ij\ldots l}{}^{(n)*}(T)$. This is most easily seen in the three-body case, which is now examined.

In Reference 4, it is shown that the three-body lifetime $Q^{(3)}$ includes contributions due to pure two-body interactions such as the lifetime of AB while C is far away. This can be taken care of by a subtraction procedure described in that paper, but it is just as legitimate to postpone the subtraction until after all the averages have been taken. After that has been done, it is easy to see that $c_{ijk}{}^{(3)*}$ includes three spurious contributions represented by the products $c_{ij}{}^{(2)}n_k$, $c_{jk}{}^{(2)}n_i$, and $c_{ik}{}^{(2)}n_j$. These can be eliminated by using the cor-

[3] B. Kahn and G. E. Uhlenbeck, Physica **5**, 399 (1938); B. Kahn, doctoral dissertation, Utrecht, 1938. See also J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), pp. 404 ff.
[4] F. T. Smith "Collision Lifetimes in Many-Body Processes," Phys. Rev. (to be published).
[5] F. T. Smith, Phys. Rev. **120**, 1058 (1960).

rected equilibrium expression

$$G_{ijk}^{(3)}(T) = G_{ijk}^{(3)*}(T) - G_{ij}^{(2)} - G_{ik}^{(2)} - G_{jk}^{(2)}. \quad (15)$$

The true concentration of the three-body complex is then

$$c_{ijk}^{(3)} = G_{ijk}^{(3)}(T) n_i n_j n_k. \quad (16)$$

Similar subtractions are needed for the higher-order equilibria:

$$G_{ijkl}^{(4)} = G_{ijkl}^{(4)*} - G_{ijk}^{(3)} - G_{ikl}^{(3)} - G_{jkl}^{(3)} - G_{ij}^{(2)}$$
$$- G_{jk}^{(2)} - G_{kl}^{(2)} - G_{ii}^{(2)} - G_{jl}^{(2)} - G_{ik}^{(2)}. \quad (17)$$

Using these equilibrium coefficients it is now possible to set down the equilibrium equations for all the collision complexes $c_{ij}^{(2)}$, $c_{ijk}^{(3)}$, $c_{ijkl}^{(4)}$, etc., as well as for all the stable species n_i. These must be combined with the chemical conservation conditions, for instance

$$n_i^0 = n_i + 2c_{ii}^{(2)} + \sum_{j \neq i} c_{ij}^{(2)} + \cdots. \quad (18)$$

Finally, these are to be supplemented by the perfect gas law in the form

$$p/kT = N = \sum_i n_i + \sum_{i \geq j} c_{ij}^{(2)} + \sum_{i \geq j \geq k} c_{ijk}^{(3)} + \cdots. \quad (19)$$

Equation (19) is a complete cluster expansion for the equation of state of real gases. It is entirely equivalent to the virial expansion, and reduces the problem to the evaluation of the collision lifetimes of the various clusters. These clusters are defined not by their spatial extent but by their lifetimes. Since the lifetime has a classical meaning, the expansion is also valid in the classical limit; the classical lifetimes may in fact give a useful approximation to the quantal ones. In the quantal case the effect of the statistics of the particles (Bose–Einstein or Fermi–Dirac) has not been explicitly included in the above argument, but it can readily be introduced in evaluating the equilibria.[3]

It is gratifying to find that this approach reduces to the Kahn–Uhlenbeck form in the case of binary atomic encounters. Their result was derived by considering the quantal density of states[3]

$$\rho_l = \frac{1}{\pi} \frac{d\delta_l}{dk} = \frac{\hbar k}{2\pi\mu} Q(E, l). \quad (20)$$

This formula may also be used now to give the density of states where inelastic collisions are possible.

It is of interest to examine one of the quantal effects that enter into the evaluation of the equilibria $G^{(n)}$. This is the existence of metastable levels inside a potential barrier. If the barrier is sufficiently thick and the levels are well separated, their effects will essentially not overlap and they can be treated as isolated Breit–Wigner resonances with a narrow half-width Γ_m and a center at E_m. The shape of Q near E_m is determined by this resonance,[1]

$$Q \cong 2\hbar\Gamma_m [(E_m - E)^2 + \Gamma_m^2]^{-1}, \quad (21)$$

and its contribution to the integral in Eq. (10) can be evaluated separately. It is

$$G_m(T) = (h^2/2\pi\mu kT)^{\frac{3}{2}} (2l+1) \exp(-E_m/kT). \quad (22)$$

Thus, the metastable states with long lives behave just as bound ones, a result that is intuitively obvious but reassuring. Except near the top of the barrier, where leakage broadens the levels unduly, it is often possible to consider these resonances separately in the statistics, leaving the rest of the integral in Eq. (10) to be evaluated by using the smooth, elastic, contribution to $Q(E)$. This elastic portion may sometimes be usefully evaluated classically. The importance of deviations from the classical behavior in the region near the top of the barrier remains to be evaluated.

B. THERMODYNAMIC FUNCTIONS

The procedure of the last section can readily be extended to give other thermodynamic properties of the gas. Of these the most accessible is the internal energy U per unit volume.

The internal energy of the gas can be considered to be divided into a perfect gas portion

$$U^{(0)} = \frac{3}{2} nkT = \frac{3}{2} p, \quad (23)$$

a portion deriving from the internal energy of the stable molecules

$$U^{(1)} = \sum_i E_i n_i^0, \quad (24)$$

and a portion due to the interactions of the various collision complexes. To obtain the average energy of a typical complex A_{ij} we must start with the differential concentration

$$\delta c_{ij} = n_i n_j g_{ij}(E, l, m_l) \delta E. \quad (25)$$

It is then convenient to write

$$\frac{\delta c_{ij}}{c_{ij}} = \frac{g_{ij} \delta E}{G_{ij}} = \frac{\delta Y_{ij}}{Y_{ij}}, \quad (26)$$

where

$$\delta Y_{ij} = h^{-1} \exp(-E/kT) Q_{ij}(E, l, m_l) \delta E, \quad (27)$$

and

$$Y_{ij} = \int dY_{ij} = h^{-1} \sum_{l, m_l} \int_0^\infty \exp(-E/kT) Q_{ij}(E, l, m_l) dE. \quad (28)$$

Then the average energy of the complex is

$$E_{ij} = Y_{ij}^{-1} \int E \, dY_{ij}, \quad (29)$$

and the total internal energy due to binary complexing is

$$U^{(2)} = \sum_{ij} E_{ij} c_{ij}. \quad (30)$$

Similar expressions apply to the higher order complexes. The total internal energy is then

$$U = U^{(0)} + U^{(1)} + U^{(2)} + \cdots \quad (31)$$

(Note that the same result would be obtained had we written

$$U^{(1)*} = \sum_i E_i n_i$$

and

$$U^{(2)*} = \sum_{ij} (E_{ij} + E_i + E_j) c_{ij},$$

etc., and summed over these.)

To get the other thermodynamic functions we observe that $Y_{ij}(T)$ is just the internal partition function for the collision complex, and that the average internal energy per complex can be expressed as

$$E_{ij} = kT^2 (\partial \ln Y_{ij} / \partial T). \quad (32)$$

In integrating the equation

$$\left(\frac{\partial S_{ij}}{\partial T} \right)_V = \frac{1}{T} \left(\frac{\partial E_{ij}}{\partial T} \right)_V \quad (33)$$

to get the entropy, it is convenient to write

$$S_{ij} = T^{-1} E_{ij} + k \ln | Y_{ij} | + S_0, \quad (34)$$

in order to take care of the cases where the collision partition function Y_{ij} may be negative.

It will be observed that Y_{ij} is in fact constructed just like other partition functions if we construe

$$\delta \omega_{ij} = h^{-1} Q_{ij}(E, l, m_l) \delta_E \quad (35)$$

as the statistical weight associated with the complex at the energy E. Bound states then are a special case in which $Q(E)$ becomes a δ function [$\Gamma \rightarrow 0$ in Eq. (21)] and $\omega = 1$. This indeed allows us to treat in a unified way all the possible situations including transient colliding pairs, long-lived metastables inside a potential barrier, excited states below the dissociation limit (with a finite radiative lifetime), and the ground state of the molecule.

It can now be seen that the equilibrium coefficient $G_{ij}(T)$ can be expressed as a ratio of partition functions. The partition function for the free species A_i is the familiar expression

$$Z_i = (2\pi m_i kT / h^2)^{\frac{3}{2}} \omega_i \exp(-E_i / kT), \quad (36)$$

where ω_i is the weight factor in case of degeneracy. The complete partition function for the complex A_{ij} is the product

$$Z_{ij} = (2\pi M_{ij} kT / h^2)^{\frac{3}{2}} \sigma_{ij}^{-1} \omega_i \omega_j \exp[-(E_i + E_j)/kT] Y_{ij}, \quad (37)$$

where $M_{ij} = m_i + m_j$ and σ_{ij} is the symmetry number ($\sigma_{ii} = 2$, $\sigma_{i \neq j} = 1$). If A_{ij} is a stable state the same expression holds since Y_{ij} reduces to $\exp(-E_{ij}/kT)$

(E_{ij} is measured relative to A_i and A_j at infinite separation, and is negative for a bound state). The equilibrium relation can now be expressed simply as

$$c_{ij} / n_i n_j = G_{ij}(T) = Z_{ij} / Z_i Z_j. \quad (38)$$

The generalization to higher order collisions is obvious.

We can now include all the states of an atomic or molecular species in a single partition function. For molecules this will include the unstable complexes along with the bound states. (The proper continuum spectrum of the molecule is now to be defined as the difference between the gross continuum and the continuum due to atoms in free flight.) In the case of the atomic species A, comprising all the states A_i, we can define the various angular momentum and spin states by a set of quantum numbers γ^a, so that any degeneracies are taken care of by a summation over γ^a. The effect of the radiative lifetime of the levels will appear in the lifetime function $Q_A(E, \gamma^a)$, which takes the form of Eq. (21) near an isolated level and becomes a δ function for nonradiating states (collisional broadening can also be taken into account, of course). The internal partition function of the atom is then

$$Z_A^{\text{int}} = \sum_{\gamma_a} \int \exp(-E/kT) h^{-1} Q_A(E, \gamma^a) dE$$

$$\approx \sum_i \omega_i^a \exp(-E_i / kT). \quad (39)$$

The approximate equality at the end holds only if ionized states can be neglected.

In the case of molecules a similar expression applies, and the integration includes bound state energies as well as the continuum. For diatomic molecules AB the set of quantum numbers γ includes γ^a, γ^b, and l, m_l for their relative motion. The energy E must now be taken from some common origin such as the ground states of A and B. The result is

$$Z_{AB}^{\text{int}} = \sum_{\gamma^{ab}} \int \exp(-E/kT) h^{-1} Q_{AB}(E, \gamma^{ab}) dE. \quad (40)$$

It will be remembered that the components $Q(E, \gamma)$ appearing in Eqs. (39) and (40) are actually the diagonal elements of the matrix $\mathbf{Q}$. These are summed over all the indices γ, thus forming the trace of the matrix. Thus we can express the internal partition functions in the compact form:

$$Z_A^{\text{int}} = \int \exp(-E/kT) h^{-1} \text{Tr} \mathbf{Q}_A(E) dE, \quad (41)$$

$$Z_{AB}^{\text{int}} = \int \exp(-E/kT) h^{-1} \text{Tr} \mathbf{Q}_{AB}(E) dE. \quad (42)$$

In the case of triatomic and larger molecules like ABC that may split into three or more fragments, the necessary subtractions discussed in Sec. A are already taken care of in the definition of the complete lifetime matrix

Q_{ABC} of reference 4. Q_{ABC} includes all the bound states of ABC, and all the collisions involving the complex ABC, both the binary processes such as AB+C and the ternary ones A+B+C. Consequently the complete internal partition function for a triatomic or polyatomic species has just the same form as for the smaller species, for example

$$Z_{ABC}^{int} = \int \exp(-E/kT) h^{-1} \, \mathrm{Tr} Q_{ABC}(E) dE. \quad (43)$$

Using these partition functions the concentrations of all the molecular species and clusters can be expressed in a concise form. The thermodynamic functions of the mixture follow immediately.

C. AN EXAMPLE: CLASSICAL HARD SPHERES

In its quantal form this version of the gaseous equation of state reduces correctly to the Kahn–Uhlenbeck formula. The theory can also be applied classically, and the hard-sphere gas provides an example of the treatment. Consider a gas of atoms of diameter σ. The collisions can be classified by their relative energy E and by the magnitude L of the angular momentum. Collision only occurs if

$$L \leq L_m(E), \quad (44)$$

where

$$L_m^2 = 2\mu E \sigma^2. \quad (45)$$

The collision lifetime is negative in this range and zero elsewhere; its magnitude is just the time the interaction-free trajectory would have taken to pass through the sphere $r \leq \sigma$,

$$\left. \begin{aligned} Q(E, L) &= -(2\mu/E)^{\frac{1}{2}} \sigma (1 - L^2/L_m^2)^{\frac{1}{2}} (L \leq L_m) \\ &= 0 \qquad\qquad\qquad (L \geq L_m). \end{aligned} \right\} \quad (46)$$

In converting the quantal expression Eq. (28) for the collision partition function to classical form, we can take advantage of spherical symmetry (independence of m_l) and make the substitution

$$\hbar^2 \sum_{l, m_l} f(l) = \hbar^2 \sum_l (2l+1) f(l) \rightarrow \int f(L) d(L^2). \quad (47)$$

Then we find

$$Y_{11} = \frac{4\pi^2}{h^3} \int_0^\infty \exp(-E/kT) \int_0^{L_m^2} Q(E, L) d(L^2) dE$$

$$= -\frac{4\pi}{3} \sigma^3 \left(\frac{2\pi\mu kT}{h^2}\right)^{\frac{3}{2}}. \quad (48)$$

In writing the expression for the equilibrium coefficient G_{11} we must remember that the two collision partners are identical, so that a symmetry factor of $\frac{1}{2}$ is needed to avoid counting the collisions twice:

$$G_{11}(T) = \frac{1}{2} (h^2/2\pi\mu kT)^{\frac{3}{2}} Y_{11}(T) = -\frac{2}{3}(\pi\sigma^3). \quad (49)$$

If we confine our attention to binary collisions, we have the conditions

$$c_{11} = n_1^2 G_{11},$$

$$n_1 = n_1^0 - 2c_{11}, \quad (50)$$

and consequently

$$n = n_1 + c_{11} = n_1^0 - c_{11} = n_1^0 + (2\pi\sigma^3/3)(n_1^0)^2 + \cdots. \quad (51)$$

This reproduces the well-known second virial coefficient for the hard-sphere gas.

Similarly we can compute the average energy of the collision dimers,

$$E_{11} = Y_{11}^{-1} \int E dY_{11} = \frac{3}{2} kT. \quad (52)$$

The internal energy density is then

$$U = \frac{3}{2} kTn + c_{11} E_{11} = \frac{3}{2} kT(n + c_{11}) = \frac{3}{2} kTn_0. \quad (53)$$

This is again the correct result, showing that the instantaneous hard-sphere collisions do not affect the energy density or the specific heat.

D. TRANSFORMATION TO THE CLASSICAL CLUSTER FORMULATION

The partition function we have derived here, Eqs. (41) to (43), has a very different appearance from the classical expression in terms of the configuration integral. Nevertheless, it is not hard to derive the usual expression from the integral over the collision lifetimes. It will suffice to show the transformation explicitly for a gas of atoms interacting through the spherically symmetric potential $V(r)$.

Classically the collision lifetime can be expressed in terms of the relative kinetic energy E and angular momentum L by the equation

$$Q(E, L^2) = 2 \lim_{R \to \infty} \left(\int_{R_{min}}^R \left\{ \frac{2}{\mu} \left[E - V(r) - \frac{L^2}{2\mu r^2} \right] \right\}^{-\frac{1}{2}} dr \right.$$

$$\left. - \int_{R_{min}'}^R \left\{ \frac{2}{\mu} \left[E - \frac{L^2}{2\mu r^2} \right] \right\}^{-\frac{1}{2}} dr \right). \quad (54)$$

Here the first integral represents the time taken to get from R to the point of closest approach, R_{min}, and the second is the corresponding time for an interaction-free collision. The square roots represent the radial velocities; R_{min} and R_{min}' are defined by the condition that the radial velocity vanishes there,

$$2\mu R_{min}^2 [E - V(R_{min})] = L^2,$$

$$2\mu R_{min}'^2 E = L^2. \quad (55)$$

Using Eq. (47), the internal part of the collision partition function becomes classically, in this case:

$$Z^{int} = 4\pi^2 \hbar^{-3} \int_0^\infty \int_0^\infty Q(E, L^2) d(L^2) \exp(-E/kT) dE.$$

$$(56)$$

The integral over $d(L^2)$ corresponds to taking the trace of Q in the quantal formulation. Q itself, by Eq. (54), involves integrals over the radial coordinate r, in which the lower limit of integration depends on L^2 and E. Nonetheless, the order of integration can be changed if the limits are changed appropriately; the condition to be observed is that the square roots must remain real. Integrating first over L^2, from 0 to a maximum depending on E and r, we find

$$\int_0^\infty Q(E, L^2)d(L^2) = 2\mu \lim_{R\to\infty} \left(\int_{R_0}^R \int_0^{L_{max}{}^2} \{2\mu r^2[E - V(r)] \right.$$

$$\left. - L^2\}^{-\frac{1}{2}} d(L^2)r dr - \int_0^R \int_0^{L'_{max}{}^2} (2\mu r^2 E - L^2)^{-\frac{1}{2}} d(L^2)r dr \right)$$

$$= 2(2\mu)^{\frac{3}{2}} \lim_{R\to\infty} \left\{ \int_{R_0}^R [E - V(r)]^{\frac{1}{2}} r^2 dr \right.$$

$$\left. - \int_0^R E^{\frac{1}{2}} r^2 dr \right\}, \quad (57)$$

where we have used the conditions

$$2\mu r^2[E - V(r)] = L_{max}{}^2, \qquad 2\mu r^2 E = L_{max}'{}^2, \qquad (58)$$

and

$$V(R_0) = E.$$

Now we can integrate over dE in Eq. (56), setting the lower limit in the first integral in E to keep $[E - V(r)]^{\frac{1}{2}}$ real:

$$Z^{int} = 8\pi^2\hbar^{-3}(2\mu)^{\frac{3}{2}} \int \left\{ \int_{V(r)}^\infty [E - V(r)]^{\frac{1}{2}} \exp(-E/kT) dE \right.$$

$$\left. - \int_0^\infty E^{\frac{1}{2}} \exp(-E/kT) dE \right\} r^2 dr$$

$$= 4\pi \left(\frac{2\pi\mu kT}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty [\exp(-V(r)/kT) - 1] r^2 dr. \quad (59)$$

If the colliding atoms are identical, the symmetry factor $\frac{1}{2}$ must be included. The final form is the familiar one involving the two-atom configuration integral.

A similar development can clearly be used to obtain the configuration integral from the lifetime expression in more general cases such as many-body collisions or collisions of molecules without spherical symmetry. In these cases the lifetime Q will depend on additional variables besides E and L^2, but it can always be written in an integral form analogous to Eq. (54). The quantal sum forming $\text{Tr } Q$ becomes a classical multiple integral over several variables. I now briefly sketch the generalization of the derivation of Eq. (59) to cover more general cases.

First, consider an encounter of two molecules without spherical symmetry and with a potential depending only on r, θ, ϕ. Q may still be written in the form of Eq. (54), with $V(r, \theta, \phi)$, but the integration in dr must be

carefully taken over the full path from the first passage into the sphere at $r = R$ to the last passage out. Instead of Eq. (47), we need now the equivalences

$$\hbar\Delta m_r \to \delta L_z = \delta(L \cos\theta) = L \sin\theta \delta\theta,$$

$$\hbar\Delta l \to \delta L. \quad (60)$$

L defines only the plane in which the motion occurs, and we must still average over the various orientations in that plane represented by the angle ϕ. As before we integrate explicitly over $L dL$ and dE, and we are left with the configuration integral over the volume element $d\tau = r^2 dr \sin\theta d\theta d\phi$.

Next, consider the three-body collision lifetime $Q^{(3)}$. In this, as in higher order collisions, r must be replaced by the generalized distance ρ which can be defined in terms of the trace of the inertia tensor for the instantaneous configuration of the three-body system with respect to the center of mass:

$$2\mu\rho^2 = \text{Tr} \mathbf{I}. \quad (61)$$

All the other relative coordinates can be written as angles. Now $Q^{(3)}$ may classically be written in a form just like Eq. (54), but using the coordinate ρ and its related velocity v_ρ. The integrals in Q are of the type $\int^R v_\rho{}^{-1} d\rho$ with

$$\frac{1}{2}\mu v_\rho{}^2 = E - V(\mathbf{q}) - \Lambda^2/2\mu\rho^2, \quad (62)$$

where Λ^2 represents the generalized angular momentum in the six-dimensional space of the relative motion.[5] To form the trace of $\mathbf{Q}$ we must sum over five angular momenta γ, which may be taken in the regular representation defined in reference 5. In this representation we define the angular momenta in successive subspaces of the six-space, getting the equivalences

$$\hbar\lambda \to \Lambda,$$

$$\hbar\lambda_4 \to \Lambda_4 = \Lambda \cos\theta_4,$$

$$\hbar\lambda_3 \to \Lambda_3 = \Lambda_4 \cos\theta_3,$$

$$\hbar\lambda_2 \to \Lambda_2 = \Lambda_3 \cos\theta_2,$$

$$\hbar\lambda_1 \to \Lambda_1 = \Lambda_2 \cos\theta_1. \quad (63)$$

The sum over γ becomes an integral over the angular momenta

$$d\Lambda d\Lambda_4 d\Lambda_3 d\Lambda_2 d\Lambda_1 = \Lambda^4 d\Lambda \cos^3\theta_4 \sin\theta_4 d\theta_4 \cos^2\theta_3 \sin\theta_3 d\theta_3$$

$$\times \cos\theta_2 \sin\theta_2 d\theta_2 \sin\theta_1 d\theta_1. \quad (64)$$

To this must be added an integration over the angle ϕ in the remaining 2-space defined by the Λ's. The integrations over $d\Lambda$ and dE can now be carried out, leaving a configuration integral in ρ and 5 angles, representing the 6 coordinates of relative motion of the three particles.

In this way, a hierarchy of configuration integrals can be obtained. They are a classical form of the ex-

pressions $G^{(n)*}$ of Eq. (12). The first two of them are

$$G^{(2)} = \int \{\exp[-V(\mathbf{r})/kT]-1\} d^3\mathbf{r},$$

$$G^{(3)*} = \int \{\exp[-V(\boldsymbol{\varrho})/kT]-1\} d^6\boldsymbol{\varrho}. \qquad (65)$$

To get the equilibrium coefficients we must perform the subtractions of Eqs. (15) and (17); for the case of identical particles we must also introduce the symmetry factor, so that the final equilibrium coefficient becomes $b_n = G^{(n)}/n!$. The quantity b_n is in fact identical with the cluster integral designated b_n in Mayer's classical theory[6]—this can easily be shown by approximating the potential by a sum of pair potentials and developing the integrand as a polynomial in f_{ij} as in Mayer's treatment. Thus the clusters defined by the n-body lifetimes turn out to be a physical realization of Mayer's clusters.

The clusters used in this treatment differ from the "physical clusters" considered by Hill,[7] which are defined by setting some boundary in phase space, and which are more easily defined when the intermolecular forces are strong. Hill's treatment requires the residual consideration of collisions between clusters, which therefore cannot be treated as a perfect gas.

E. CONCLUSIONS

Starting from the simple assumption that gas imperfections can be attributed to the formation of transient complexes that can be treated just like stable molecules, we have arrived at results of unexpected generality. The lifetime matrix $\mathbf{Q}$ for each atomic or molecular species can be extended to include the bound states as well as the collisional continuum for which it was originally introduced. A new, more general form for the molecular internal partition function has been discovered,

$$Z^{\text{int}} = \int \exp(-E/kT) h^{-1} \text{Tr}\mathbf{Q}(E) dE, \qquad (66)$$

which reduces, for bound states, to the familiar form. For an atomic gas, it reduces to the Kahn–Uhlenbeck expression for the quantal second virial coefficient; in the classical limit it can be transformed to the usual configuration integral. All possible molecular combinations, including nonbonding systems that may even have negative partition functions and concentrations, must be considered as present in the gas. Using the partition functions, the concentrations and the thermodynamic functions can be immediately expressed. The result is equivalent to an exact quantal cluster expansion, and the transition to the classical limit follows simply and directly by introducing the classical collision lifetimes.

The principal formal deficiency of the theory in its present form is that it does not cope with the long-range Coulomb interaction.

The effectiveness of the lifetime matrix in dealing with the thermodynamic properties of gases leads to the hope that it may also be useful in connection with transport properties. It is well known that the usual derivation of the Boltzmann equation neglects the duration of the collisions.

It now becomes important to seek practical methods for calculating the lifetime matrix or its trace. Percival's work[8] in this direction is welcome.

[6] J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940).

[7] T. L. Hill, J. Chem. Phys. **23**, 617 (1955); T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), pp. 152 ff; N. Davidson, *Statistical Mechanics*, (McGraw-Hill Book Company, Inc., New York, 1962), pp. 337 ff.

[8] I. A. Percival Proc. Phys. Soc. (London) **80**, 1290 (1962).